

# A Novel Production Route for Nylon-6:

## Aspects of Catalysis and Process Development

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**Summary:** A novel production route for nylon-6 out of 6-aminocapronitrile has been investigated. Hydrolysis of 6-aminocapronitrile using a solid porous ZrO<sub>2</sub> catalyst is the key step in this novel route. Nylon-6 with a number average molecular weight of  $10 \cdot 10^3 \text{ g} \cdot \text{mol}^{-1}$  can be produced from the hydrolyzed 6-aminocapronitrile. The reactor set up for the polycondensation can in broad outline be the same as the continuously operated reactor used for the  $\epsilon$ -caprolactam based production of nylon-6. For the hydrolysis of 6-aminocapronitrile a number of parallel batchwise operated loop reactors is recommended. A fixed bed of catalyst particles is part of each recirculation loop. Intraparticle mass transport limitation can be avoided by using catalyst particles made of a shell of active ZrO<sub>2</sub> and a massive inert core. An annual production of  $50 \cdot 10^6 \text{ kg}$  nylon-6 demands for  $5.3 \text{ m}^3$  zirconia.

**Keywords:** 6-aminocapronitrile; batchwise operated fixed bed loop reactor; nitrile hydrolysis; polycondensation; porous ZrO<sub>2</sub> catalyst

### Introduction

Almost all commercial nylon-6 is produced by consecutive manufacturing of the intermediates cyclohexanone oxime and caprolactam from the raw material benzene, see Figure 1.

The disadvantages of the present process route from benzene to nylon-6 are yield loss, resulting from an incomplete selectivity and yield of the various process steps, as well as the use of the explosive and expensive hydroxylamine in the production of cyclohexanone oxime out of cyclohexanone, i.e. step 3 in Figure 1. Moreover, large amounts of the side product ammonium sulphate are formed.

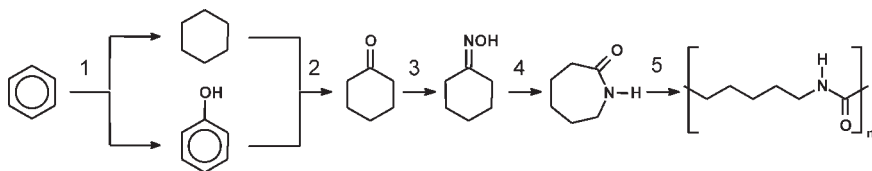
An interesting alternative for the present  $\epsilon$ -caprolactam-based production route of nylon-6 is production out of 1,3-butadiene. The intermediate 6-aminocapronitrile can be prepared by hydrocyanation of 1,3-butadiene followed by selective hydrogenation, see Figure 2.

This 3-step route to nylon-6 as represented in Figure 2 may be advantageous over the present 5 step  $\epsilon$ -caprolactam based production as a result of a considerably better atom efficiency and less energy consumption.

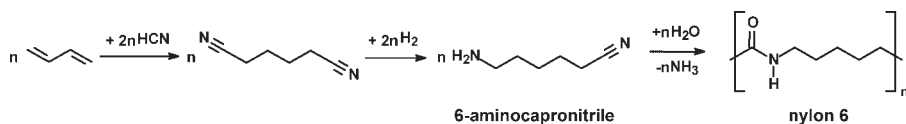
Transformation of 6-aminocapronitrile into high molecular weight nylon-6 demands for *complete* hydrolysis of the nitrile groups into the corresponding monomeric amide or carboxylate. Residual nitrile groups act as chain stoppers in the subsequent step polymerization and hamper building up of the molecular weight of the polymer. We demonstrated that *complete* hydrolysis of 6-aminocapronitrile is possible using a porous zirconia catalyst.<sup>[1]</sup> Side products were not formed. The global reactions for the production of nylon-6 out of 6-aminocapronitrile are shown in Figure 3.

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**Figure 1.**

$\epsilon$ -caprolactam based production of nylon-6 out of benzene.

**Figure 2.**

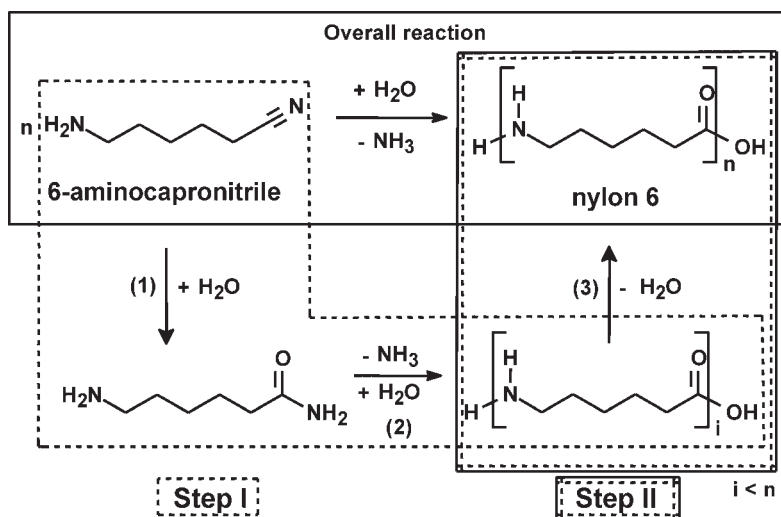
Process steps for the formation of nylon-6 from 1,3-butadiene.

Figure 3 demonstrates that production of nylon-6 out of 6-aminocapronitrile can roughly be divided into two major parts:

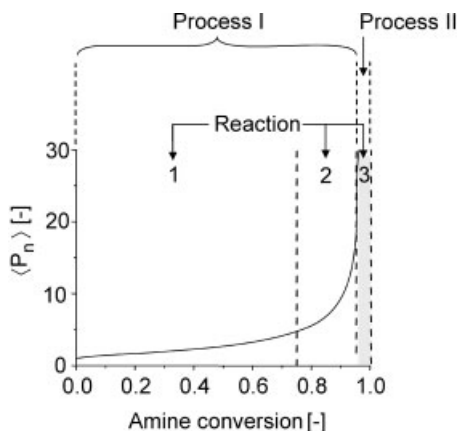
I: Complete porous zirconia ( $\text{ZrO}_2$ ) catalyzed selective nitrile hydrolysis and amide amidation, i.e. reactions (1) and (2) in Figure 3, respectively. Note that, depending on the amine conversion, oligomer formation may be significant, see Figure 4.<sup>[2]</sup>

II: Polycondensation of the completely hydrolyzed 6-aminocapronitrile and its oligomers to nylon-6, i.e. reaction (3) in Figure 3.

Results of zirconia catalyzed nitrile hydrolysis as well as the performance of polycondensation of the completely hydrolyzed 6-aminocapronitrile in terms of the molecular weight will be presented in this paper. Additionally some critical process

**Figure 3.**

Overall reaction of the production of nylon-6 out of 6-aminocapronitrile. (1): global nitrile hydrolysis reaction; (2) amide hydrolysis and oligomer formation; (3): poly amide formation.



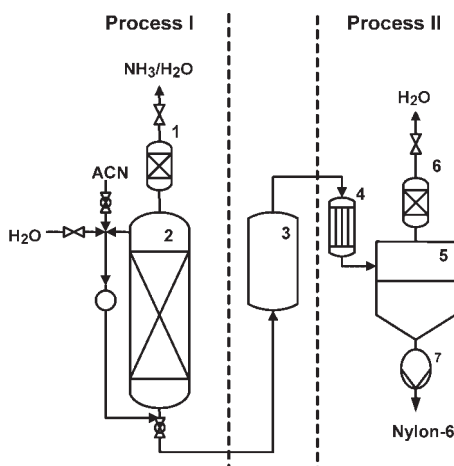
**Figure 4.** Development of the number average degree of polymerization ( $\langle P_n \rangle$ ) with amine conversion related to the reactions presented in Figure 3 and the process operation given in Figure 5.

design aspects will be discussed. These design aspects are based on an annual production of  $50 \cdot 10^6$  kg nylon-6, which is a proper amount for an engineering plastic production plant.

## Conceptual Process Configuration

The requirements for complete conversion of the 6-aminocapronitrile hydrolysis as well as for the amine amidation, i.e. the actual polymerization, are in contradiction. Hydrolysis needs water while in the actual polycondensation, i.e. reaction (3) in Figure 3, water is a reaction product which has to be removed from the reaction mixture to allow molecular weight build up. As a consequence 6-aminocapronitrile hydrolysis and polymerization must be performed in two separate process steps, see Figure 5.

Note that patented process configurations also comprise two separate steps. However, a detailed elaboration of these processes has not been reported in the related patents.<sup>[3–5]</sup> The reactor for the 6-aminocapronitrile hydrolysis is a batchwise operated solid-liquid fixed bed reactor with recirculation of the reaction mixture. Note that a batchwise operated slurry reactor is not con-

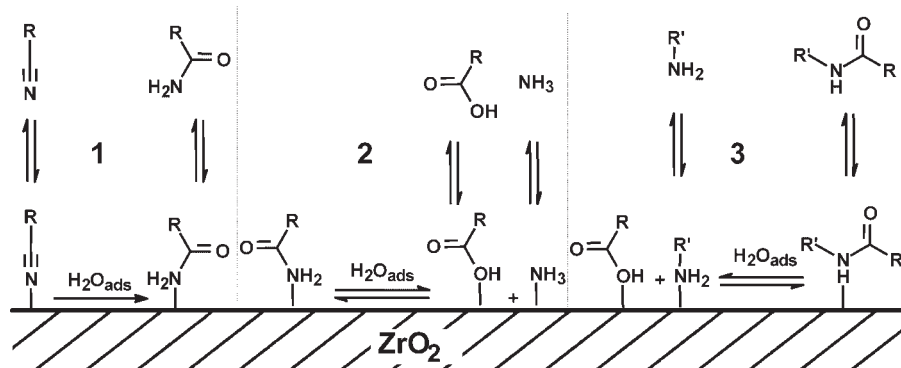


**Figure 5.** Schematic view of a two step process for the nylon-6 production out of 6-aminocapronitrile (ACN). 1: gas/liquid separator; 2: catalytic hydrolysis reactor; 3: buffer vessel; 4: evaporator; 5: polymerization stage; 6: water separator; 7: pump.

sidered, because separation of the small  $\text{ZrO}_2$  catalyst particles from the reaction product is expected to be strongly hampered by the relatively high viscosity of the product. Since ammonia is a reaction product of the amide hydrolysis as well as of the amide amidation, i.e. reaction (2) in Figure 3, completion of the hydrolysis demands for removal of  $\text{NH}_3$  in a gas-liquid separation unit, see part 1 in Figure 5.

The completely hydrolyzed 6-aminocapronitrile is transferred to a buffer vessel to allow a constant composition feed to the continuously operated polymerization reactor. Polymerization, i.e. process II in Figure 5, can be carried out in an approximately similar way as the polymerization of partially hydrolyzed  $\epsilon$ -caprolactam. Note that at the operational conditions of the polymerization, ring closure of a significant part the hydrolyzed 6-aminocapronitrile leads to  $\epsilon$ -caprolactam, the actual monomer of nylon-6.<sup>[6–8]</sup> Nylon-6 formation actually proceeds via two parallel routes, i.e. ring opening polymerization of  $\epsilon$ -caprolactam and polycondensation of the hydrolyzed 6-aminocapronitrile.

The continuous production of nylon-6 out of  $\epsilon$ -caprolactam can be mathematically



**Figure 6.**

Reactions on a  $\text{ZrO}_2$  surface during the formation of an N-alkyl amide out of a nitrile, a primary amine and water. 1: Nitrile hydrolysis; 2: Amide hydrolysis into a carboxylic group; 3: Carboxylic acid amidation.<sup>[9]</sup>

described as polymerization in a plug flow reactor. An alternative option for the actual polymerization reactor will be discussed very shortly at the end of this paper.

However, development of a technically and economically viable process for the complete hydrolysis of 6-aminocapronitrile is the most challenging part of the novel route to nylon-6 as presented in the Figure 2 and 3.

### Zirconia Catalyzed Nitrile Hydrolysis and Amine Amidation

Figure 6 shows the fundamental reaction steps for the nitrile hydrolysis on a zirconia surface.

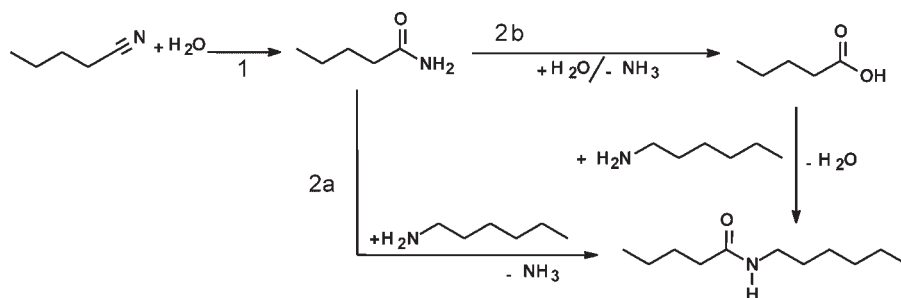
Figure 6 clearly demonstrates that the nitrile hydrolysis, the amide hydrolysis into

a carboxylic group, as well as the amine amidation are all catalyzed by  $\text{ZrO}_2$ .

Nitrile hydrolysis and consecutive coupling with aliphatic linear amine was studied for the model reaction system n-pentanenitrile and n-hexylamine, see Figure 7. So selectivity measurements are not hampered by oligomerization of the hydrolysis product, see reaction (2) in Figure 3.

The hydrolysis reaction was carried out at various temperatures and in the presence of twofold excess of water related to n-pentanenitrile in the presence of porous  $\text{ZrO}_2$ . The reactions were started with exactly equimolar amounts of n-pentanenitrile and n-hexylamine. No solvent was used.

Experimental results revealed that the performance of  $\text{ZrO}_2$  regarding to n-pentanenitrile conversion and selectivity towards the desired reaction products was



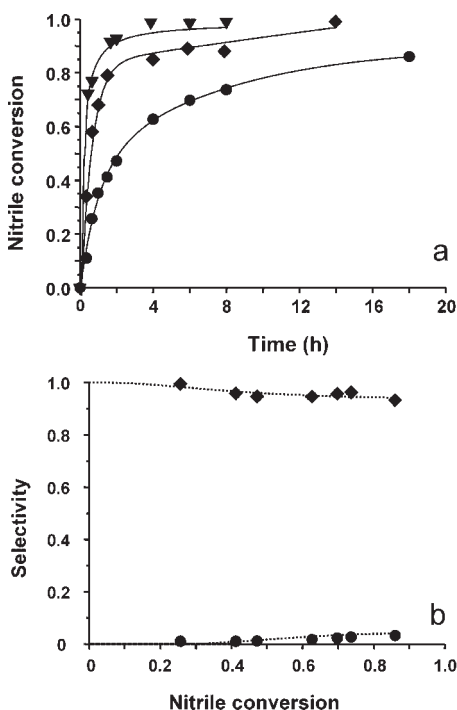
**Figure 7.**

Reaction for the hydrolysis of n-pentanenitrile and subsequent coupling of the reaction products with n-hexylamine to n-hexylpentanamide.

superior with respect to  $\text{TiO}_2$  and  $\text{Nb}_2\text{O}_5$ . Experimental results for the  $\text{ZrO}_2$  catalyst regarding conversion and selectivity are collected in Figure 8.

The results show complete nitrile conversion at 230 °C in four hours reaction time.

Considering the results of the hydrolysis of n-pentanenitrile in the presence of an equimolar amount of n-hexylamine, also a *complete* and *fully selective* hydrolysis of 6-aminocapronitrile using a porous  $\text{ZrO}_2$  catalyst can be expected. This is supported by the results of a study of the reaction product of the  $\text{ZrO}_2$  catalyzed hydrolysis of 6-aminocapronitrile at 230 °C with infrared spectroscopy. The reaction product did not show a characteristic nitrile infrared absorption band.<sup>[1]</sup> These observations strongly



**Figure 8.**

a: Conversion time history for the  $\text{ZrO}_2$  catalysed hydrolysis of n-pentanenitrile in the presence of n-hexylamine (n-pentanenitrile: 0.71 g (8.6 mmol); n-hexylamine: 0.87 g (8.6 mmol); water: 0.31 g (17.2 mmol);  $\text{ZrO}_2$ : 0.2 g) ●: 180 °C; ◆: 210 °C; ▼: 230 °C. b: Selectivity development for pentanamide (●) and n-hexylpentanamide (◆) at 180 °C.

support the assumption that the reaction mixture resulting after the hydrolysis of 6-aminocapronitrile may be considered to be a proper starting material for the polymerization to nylon-6.

## The Polymerization of Completely Hydrolyzed 6-aminocapronitrile

The polymerization of hydrolyzed 6-aminocapronitrile in the presence of  $\text{ZrO}_2$  has been studied at 230 °C with various initial molar ratios of 6-aminocapronitrile and water. The results are collected in Table 1. The results in Table 1 clearly demonstrate that the number average molecular weight does not come into the required molecular weight range of  $10 \cdot 10^3$ – $15 \cdot 10^3 \text{ g} \cdot \text{mol}^{-1}$  for commercial nylon-6. Molecular weight build up is probably hampered by the presence of water, which is a reaction product in the actual polymerization, see reaction (3) of step II in Figure 3. This suppression of the molecular weight build up by water is supported by the results of melt post-condensation with water removal at 250 °C of the product of polymerization of the completely hydrolyzed 6-aminocapronitrile, i.e. the isolated material reflected in the first

**Table 1.**

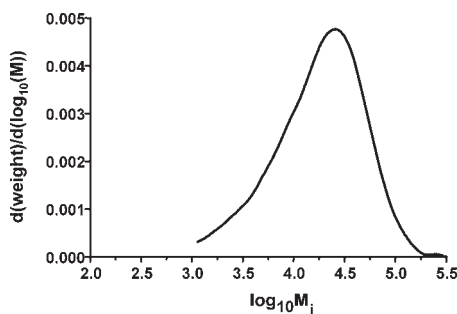
The molar mass distribution<sup>a)</sup> of the nylon-6 synthesized from 6-aminocapronitrile, using  $\text{ZrO}_2$  as the catalyst.

ACN <sup>b)</sup> :H <sub>2</sub> O	$M_n [\text{g} \cdot \text{mol}^{-1}]$	PDI [–]
1:2	4 100	1.4
1:2 <sup>c)</sup>	4 700	2.6
1:4	4 000	1.4
1:8	4 000	1.5
1:10	3 900	1.4

a) the molecular mass distribution was determined using Size Exclusion Chromatography (SEC) with hexafluoroisopropanol as eluent. The set-up was equipped with a two-column set (PSS, PFG Linear xl 7  $\mu\text{m}$  8  $\times$  300 mm) in series and a differential refractive-index detector. Calibration was based on poly methyl methacrylate samples with a narrow polydispersity (Polymer Laboratories). For further details, see van Dijk et al.[1];

b) 6-aminocapronitrile;

c) nylon-6 of the first row after 24 hours post-condensation at 185 °C in the solid state.



**Figure 9.**

Normalized molecular mass distribution of the product of the melt post-condensation at 250 °C of the isolated material as mentioned in the first data row in Table 1. Polydispersity index (PDI) of this melt post-condensation product: 2.6.

data row in Table 1. Figure 9 shows the molecular weight distribution of this melt post-condensation product.

The number average molecular weight of the melt condensation product just falls inside the required  $M_n$  range of  $10 \cdot 10^3$ – $15 \cdot 10^3$  g · mol<sup>-1</sup> for commercial nylon-6.

The results of melt condensation demonstrate that the ZrO<sub>2</sub> catalyzed hydrolysis of 6-aminocapronitrile leads to an intermediate product, which is well suitable for the production of nylon-6 with a proper molecular weight for commercial application.

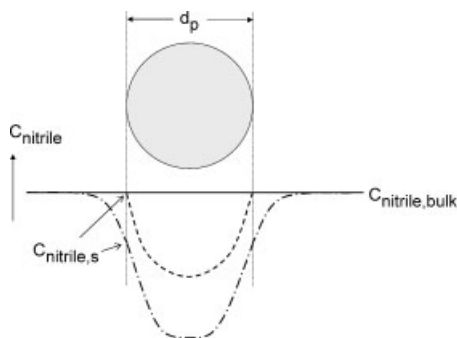
### Catalyst and Reactor Design for the ZrO<sub>2</sub> Catalyzed Hydrolysis of 6-aminocapronitrile

All considerations in this section are based on a recipe with a 1:2 molar ratio of 6-aminocapronitrile (C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>, 0.1122 kg/mol) and water (0.018 kg/mol). Note that a limited part of the excess amount of water is consumed during the consecutive partial amide hydrolysis into a carboxylic group. The remaining water is used for the removal of ammonia, see Figure 5. Ammonia is a reaction product of the amide hydrolysis as well as of the amine amidation reaction leading to oligomers, see reaction (2) in Figure 3. In order to limit the reaction

time for complete nitrile hydrolysis in Process I to 4 hours, design considerations are based on a reaction temperature of 250 °C.

To the best of the authors' knowledge, detailed kinetic models of the ZrO<sub>2</sub> catalyzed hydrolysis of either n-pentanenitrile or 6-aminocapronitrile are not reported in literature. Note that the molecular weight build up at high 6-aminocapronitrile conversions hampers the determination of rate constants of the fundamental reaction steps proceeding at the catalyst surface. All considerations presented in this section are therefore based on global kinetic insights obtained for the hydrolysis of n-pentanenitrile in the presence of n-hexylamine. The hydrolysis of 6-aminocapronitrile is assumed to obey zero order kinetics in substrate for conversions up to 80%. All active sites are then occupied by 6-aminocapronitrile, intermediate products and water, see Figure 6. For conversions above 80% first order kinetics in substrate is supposed. The amount of water in the reaction mixture up to a complete 6-aminocapronitrile conversion is assumed to be high enough to guarantee zero order kinetics with respect to water, i.e. occupation of the relevant catalyst sites with water is still complete. These starting points for the kinetics are supported by the results for the hydrolysis of n-pentanenitrile at 230 °C as collected in Figure 8(a). Because the 6-aminocapronitrile hydrolysis is catalyzed by porous solid ZrO<sub>2</sub> particles, reaction rates may be limited by transport of the reactants and products to and from the active catalyst sites, i.e. inter- and intra-particle transport resistances may limit the rate of hydrolysis, see Figure 10.

Rate coefficients at 250 °C were obtained from the corresponding rate coefficients of the n-pentanamide hydrolysis in the low and high conversion region for reactions at 180 °C, 210 °C and 230 °C by extrapolation using Arrhenius' law. Intra-particle diffusion limitation for the small scale batch reactions with 5 μm ZrO<sub>2</sub> particles can be excluded: plots of the observed rate coefficients as a function of



**Figure 10.**

Concentration profiles around a porous catalyst particle: —: no transport limitations (intrinsic kinetics); -----: only intraparticle diffusion limitation; - · - · - · -: interparticle and intraparticle transport limitation.

temperature according to Arrhenius' law did not point to any decrease of the activation energy at higher temperatures. Such a decrease of the (apparent) activation energy is typical for intraparticle diffusion limitation.<sup>[10]</sup> Rate coefficients are based on the mass balance for the nitrile:

$$-V_l \cdot \frac{dC_{\text{nitrile}}}{dt} = k_n^v \cdot C_{\text{nitrile}}^n \cdot V_{\text{cat}} \quad (1)$$

In Equation (1)  $V_l$ ,  $V_{\text{cat}}$ ,  $C_{\text{nitrile}}$ ,  $n$  and  $k_n^v$  respectively stand for the volume of the liquid phase, the catalyst volume, the nitrile concentration in the liquid phase, the reaction order and the rate coefficient based on the reaction rate per  $\text{m}^3$  catalyst. Rate coefficients and activation energies are collected in Table 2. An annual production of  $50 \cdot 10^6$  kg nylon-6 demands for about  $5.3 \text{ m}^3$   $\text{ZrO}_2$  catalyst. This estimation is based on intrinsic kinetics and 8000 operation hours per annum. Intrinsic kinetics is approximately obeyed in the complete conversion range when a

spherical shell catalyst is used. The porous  $\text{ZrO}_2$  shell is fixed on a non porous inert core. The shell dimensions for intrinsic kinetics are estimated from the Thiele modulus ( $\phi$ ) for simple order irreversible reactions:<sup>[10]</sup>

$$\phi = \delta \cdot \sqrt{\frac{n+1}{2} \cdot \frac{k_n^v \cdot C_{\text{nitrile},s}^{n-1}}{D_{\text{nitrile},\text{eff}}}} \quad (2)$$

In Equation (2)  $\delta$ ,  $C_{\text{nitrile},s}$   $D_{\text{nitrile},\text{eff}}$  stand for the thickness of the shell, the concentration of 6-aminocapronitrile at the outer surface of the porous  $\text{ZrO}_2$  shell and the effective diffusion coefficient of the nitrile in the catalyst pores, respectively. Note that pore diffusion limitation is negligible for  $\phi \leq 1$  and  $\phi < 0.3$  when respectively zero and first order kinetics is obeyed.

The relevant parameters used for the estimation of the shell thickness are given in Table 3.

The intrinsic rate coefficients, together with the effective diffusion coefficient and the concentration of 6-aminocapronitrile at the outer surface of the  $\text{ZrO}_2$  shell allow the estimation of the highest value of the  $\text{ZrO}_2$  shell thickness for which the influence of diffusion in the catalyst pores is just negligible during the complete course of the hydrolysis reaction. Using Equation (2) together with the values for  $k_n^v$ ,  $D_{\text{nitrile},\text{eff}}$  and  $C_{\text{nitrile},s}$  from the Table 2 and 3, a proper active  $\text{ZrO}_2$  shell thickness  $\delta$  is calculated to be  $0.3 \cdot 10^{-3} \text{ m}$ .

Using a particle size of  $5 \cdot 10^{-3} \text{ m}$  in the recycle loop reactor, the total particle volume necessary is  $14.7 \text{ m}^3$ . For a bed porosity  $\varepsilon_b$  of about 0.5 a total reactor volume of  $30 \text{ m}^3$  is necessary for an annual production of  $50 \cdot 10^6$  kg nylon-6. Note that a 6-aminocapronitrile conversion of 80% is already reached in 20–25 minutes. The

**Table 2.**

Rate coefficients of the hydrolysis of n-pentanenitrile at  $250^\circ\text{C}$  based on reaction rates per  $\text{m}^3$   $\text{ZrO}_2$  catalyst<sup>a)</sup> extrapolated from rate data at  $180^\circ\text{C}$ ,  $210^\circ\text{C}$  and  $230^\circ\text{C}$ .

Conversion range (%)	$r_{\text{nitrile}}^v$ ( $\text{mol} \cdot \text{m}_{\text{cat}}^{-3} \cdot \text{s}^{-1}$ )	$n$	$k_n^v$	Activation energy (kJ/mol nitrile)
0–80	$k_0^v$	0	$25 (\text{mol} \cdot \text{m}_{\text{cat}}^{-3} \cdot \text{s}^{-1})$	55.8
>80	$k_1^v \cdot C_{\text{nitrile}}$	1	$2.2 \cdot 10^{-3} (\text{s}^{-1})$	60.0

<sup>a)</sup> Internal catalyst surface  $288 \text{ m}^2/\text{g}$  (by BET analysis).



**Table 3.**

Molecular and effective diffusion coefficient as well as the concentration of 6-aminocapronitrile at the outer surface of the porous ZrO<sub>2</sub> shell.

Conversion range (%)	D <sub>nitrite</sub> <sup>a)</sup>	D <sub>nitrite,eff</sub> <sup>b)</sup>	C <sub>nitrite,s</sub> <sup>c)</sup>
	(m <sup>2</sup> /s)	(m <sup>2</sup> /s)	(mol/m <sup>3</sup> )
0–80	10 <sup>−8</sup>	10 <sup>−9</sup>	6.1 · 10 <sup>3</sup> → 1.2 · 10 <sup>3</sup>
>80	10 <sup>−9</sup>	10 <sup>−10</sup>	<1.2 · 10 <sup>3</sup>

a) At 250 °C, as a result of oligomer formation at higher conversions, see the Figure 3 and 4, the viscosity increases and by that the diffusivity decreases;<sup>[11]</sup>

b) Effective diffusion coefficient estimated from the molecular diffusion coefficient D<sub>mol</sub> by

$$D_{\text{eff}} = \frac{\varepsilon}{\tau} \cdot D_{\text{mol}} \quad (3),$$

using a void fraction  $\varepsilon$  in the ZrO<sub>2</sub> shell of 0.3 and a tortuosity factor  $\tau$  of 3;<sup>[10]</sup>

c) The resistance against mass transfer from the bulk liquid to the outer particle surface of the porous ZrO<sub>2</sub> shell is assumed to be negligible. This assumption is validated after global reactor design.

additional 3.5 hours are necessary to increase the conversion up to 99.8%. In this study the total amount of particles is equally divided over 20 parallel loop reactors, each with a volume of 1.5 m<sup>3</sup>. This reactor configuration makes the 6-aminocapronitrile hydrolysis unit rather insensitive for technical failure. Proper scheduling of the start of the reaction in each reactor ensures a more or less constant feed rate of the hydrolysis product to the buffer vessel preceding the polymerization reactor, see Figure 5.

Relevant parameters for an estimation of the resistance against mass transfer from the bulk liquid to the outer surface of the catalyst particles and the pressure drop in the fixed bed loop reactor are collected in Table 4.

The liquid-particle mass transfer resistance is estimated using the relation reported by Thoenes and Kramers for mass transfer in packed bed reactors:<sup>[12]</sup>

$$\frac{k_{\text{ls}} \cdot d_p}{D_{\text{nitrite}}} \cdot \frac{\varepsilon_b}{(1 - \varepsilon_b)} = 1.0 \cdot \left( \frac{v_0 \cdot d_p \cdot \rho}{\mu \cdot (1 - \varepsilon_b)} \right)^{0.5} \cdot \left( \frac{\mu}{\rho \cdot D_{\text{nitrite}}} \right)^{1/3} \quad (4)$$

**Table 4.**

Parameters used for estimation of the liquid-particle mass transfer resistance and the pressure drop in a tubular loop reactor.

Reactor volume	V <sub>r</sub> [m <sup>3</sup> ]	1.5
Internal tube diameter	d <sub>i</sub> [m]	0.25
Reactor length	L [m]	30.56
Particle diameter	d <sub>p</sub> [m]	5 · 10 <sup>−3</sup>
Bed porosity	ε <sub>b</sub>	0.5
Superficial liquid velocity	v <sub>0</sub> [m/s]	0.1
Fluid viscosity (conversion <80%)	μ <sub>1</sub> [Pa · s]	10 <sup>−4</sup>
Fluid viscosity (conversion >80%)	μ <sub>2</sub> [Pa · s]	10 <sup>−3</sup>
Density reaction mixture	ρ [kg/m <sup>3</sup> ]	904.3

In Equation (4) k<sub>ls</sub> stands for the liquid-solid mass transfer coefficient. The resistance against mass transfer is considerably smaller than the resistance against reaction for both conversion regions considered, see Table 5.

The pressure drop (ΔP) in one recycle loop reactor is estimated using the Ergun relation:

$$\Delta P = 150 \cdot \frac{(1 - \varepsilon_b)^2 \cdot \mu \cdot v_0 \cdot L}{\varepsilon_b^3 \cdot d_p^2} + 1.75 \cdot \frac{(1 - \varepsilon_b)}{\varepsilon_b^3} \cdot \frac{\rho \cdot v_0^2 \cdot L}{d_p} \quad (5)$$

The pressure drop calculated for the last stage of the reaction, i.e. for conversions higher than 80%, is 4.3 bar corresponding with an energy dissipation rate, i.e. necessary recycle pump shaft work, of about 2.2 · 10<sup>3</sup> Watt per loop reactor. The gas liquid separator for the removal of ammonia should be positioned just before the suction point of the recycle pump, because of the relatively low pressure at this position.

The results of the global calculations presented in this section demonstrate that a number of parallel batchwise operated fixed bed loop reactors is a promising reactor configuration for complete and selective hydrolysis of 6-aminocapronitrile.

## Production of Nylon-6 out of the Hydrolysis Product of 6-aminocapronitrile

In the actual polymerization step of the completely hydrolyzed 6-aminocapronitrile,



**Table 5.**

Resistances against fluid-particle mass transfer and reaction.

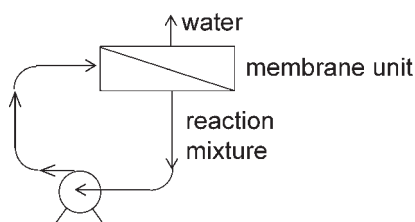
Conversion range	$k_{ls}$	Mass transfer resistance	Resistance against Reaction <sup>a)</sup>	Resistance against reaction
[%]	$[10^{-6} \text{ m/s}]$	$\frac{d_p}{6 \cdot k_{ls}} [\text{s}]$	$\frac{C_{\text{nitrile}}}{f_{\text{cat}} \cdot k_0} [\text{s}]$	$\frac{1}{f_{\text{cat}} \cdot k_1} [\text{s}]$
0–80	424	2	678 (0%) 68 (80%)	
>80	62	13.4		1262

<sup>a)</sup>  $f_{\text{cat}}$  is the fraction of the particle consisting of the active  $\text{ZrO}_2$  shell ( $f_{\text{cat}} = 0.36$ ).

100% water removal is a key issue for proper molecular weight build up. Besides the reactor configuration in Figure 5, process II, a process concept based on water removal by pervaporation with a membrane may be an interesting option.<sup>[13,14]</sup>

As a result of the high reaction temperature the water activity in the reaction mixture is expected to be relatively high and reasonable water fluxes through the membrane may be possible. For the pervaporation option a number of parallel batchwise operated loop reactors seems to be a proper choice, see Figure 11.

The retentate of the membrane is recycled in the loop. As a result of the high viscosities the resistance against mass transfer to the membrane surface may be a complicating factor. Fast surface renewal by relatively high flow rates resulting from recirculation may reduce the mass transfer resistance. Note that as a result of the high viscosity of the reaction mixture the flow is laminar. Structured internals are necessary to ensure fast refreshment of the membrane surface. Also fouling of the membrane is a key issue.

**Figure 11.**

Schematic representation of the polymerization using a pervaporation membrane for water removal.

## Conclusions

- Hydrolysis of n-pentanenitrile is possible with complete conversion and complete selectivity towards pentanamide and pentanoic acid (see reaction 1 and reaction 2b in Figure 7) within 4 hours using a porous  $\text{ZrO}_2$  catalyst.
- Nylon-6 can be produced from completely hydrolyzed 6-aminocapronitrile with a number average molecular weight of  $10 \cdot 10^3 \text{ g} \cdot \text{mol}^{-1}$ , which is sufficient for many technical applications.
- Catalyst particles based on a porous  $\text{ZrO}_2$  shell and a massive inert core are suitable for 6-aminocapronitrile hydrolysis in a batchwise operated fixed bed loop reactor. Reaction rates are not limited by mass transport for catalyst particles of  $5 \cdot 10^{-3} \text{ m}$  and a  $\text{ZrO}_2$  shell thickness of  $0.3 \cdot 10^{-3} \text{ m}$ .

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